

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

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16 GIU. 2004	
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NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing
(day/month/year)

14.06.2004

Applicant's or agent's file reference
3160PTWO/AG/1a

IMPORTANT NOTIFICATION

International application No.
PCT/EP 03/02281

International filing date (day/month/year)
06.03.2003

Priority date (day/month/year)
08.03.2002

Applicant
COLOROBIA ITALIA S.P.A. et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

Name and mailing address of the international preliminary examining authority:



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PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

REC'D 15 JUN 2004


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Applicant's or agent's file reference 3160PTWO/AG/1a		FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)	
International application No. PCT/EP 03/02281	International filing date (day/month/year) 06.03.2003	Priority date (day/month/year) 08.03.2002	
International Patent Classification (IPC) or both national classification and IPC C09C1/00, C09C1/00			
Applicant COLOROBIA ITALIA S.P.A. et al.			

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 6 sheets, including this cover sheet.
 - ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 2 sheets.

3. This report contains indications relating to the following items:
 - I ☒ Basis of the opinion
 - II ☐ Priority
 - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - IV ☐ Lack of unity of invention
 - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - VI ☐ Certain documents cited
 - VII ☐ Certain defects in the international application
 - VIII ☐ Certain observations on the international application

Date of submission of the demand 07.10.2003	Date of completion of this report 14.06.2004
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Nobis, B Telephone No. +49 89 2399-8140



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/EP 03/02281

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1-14 as originally filed

Claims, Numbers

12, 13 as originally filed

1-11 filed with telefax on 25.03.2004.

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☒ the claims, Nos.: 12,13
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/EP 03/02281**

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes: Claims	1-4,6,7,9-11
	No: Claims	5,8
Inventive step (IS)	Yes: Claims	1-4,6,7,9-11
	No: Claims	5,8
Industrial applicability (IA)	Yes: Claims	1-11
	No: Claims	

2. Citations and explanations

see separate sheet

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1: US6228160

D2: US4448608

D3: US4289745

D4: US4292294

Prior art

D1 (US6228160) discloses colorant particles, e.g. Fe_3O_4 having a preferred particle size of less than 30 nm, in particular about 20 nm, which are used for coloring ceramic compositions.

D2 (US4448608) discloses a coloured inorganic complex of stannous oxide with titanium and zinc oxides ($(\text{TiO}_2)_n\text{SnO} \cdot \text{ZnO}$) suitable for use as a colouring pigment for ceramics, having particle dimensions in the nanometer range (c. 4 l. 25-29).

D3 (US4289745) discloses a spinel (e.g. MnFe_2O_4 ; c. 3 l. 22-56) with particle size 0.1 micron (= 100 nm) produced by a wet precipitation process wherein the obtained suspension is subsequently dried.

D4 (US4292294) discloses a spinel (e.g. ZnFe_2O_4 ; c. 1 l. 67 – c. 2 l. 4) with particle size 0.1 micron (= 100 nm) produced by a wet precipitation process wherein the obtained suspension is subsequently filtered and dried.

Novelty

Product claims 1 to 4:

There is no disclosure in the prior art of a ceramic colorant as defined in claim 1, in particular in which the solvent of the suspension is a high-boiling alcohol. Therefore, novelty is acknowledged for the subject-matter of claim 1 and of claims 2 to 4 which are dependent thereof.

Process claim 5:

Claim 5 relates to a process which may lead to products other than the ceramic colorants in the form of suspensions as defined in claim 1, i.e. the last (optional) process step foresees drying of the precipitate after centrifugation.

In the light of D3 and D4 novelty cannot be acknowledged for the subject-matter of claim 5.

Process claim 6:

Claim 6 further defines the process of claim 5. The additional process steps of rapid addition of the reagents bringing to room temperature and dehydration are not disclosed in the prior art, therefore novelty is acknowledged for the subject-matter of claim 6.

Process claim 7:

Novelty is also acknowledged for the subject-matter of claim 7, which is a process for the preparation of the novel ceramic colorants of claims 1 to 4.

Product claim 8:

Claim 8 claims colorants according to claims 1 and 2 in the form of powders. Applicant's reply dated 25.3.2004 to the first Written Opinion has been carefully considered. Applicant has explained therein, that the claimed particles permit a control of nanocrystal dimensions and crystalline phase when obtained by calcination of the suspension of particles. However, none of the process claim 5 to 7 defines calcination as the method of choice. The suspension is merely „dried“. Therefore, the argumentation given in applicant's letter has to be considered as irrelevant for the assessment of novelty and inventive step of claim 8 as currently on file. D1, D2, D3 and D4 each disclose such a colorant in the form of a powder, consequently novelty cannot be acknowledged for the subject-matter of claim 8.

Use claims 9 to 11:

The product of claims 1 to 4 is regarded as novel, consequently any use of such a product is also novel.

Inventive step

The technical problem underlying the present application can be seen in providing a colorant for ceramics guaranteeing a constancy in colour, allowing to obtain a wide range of shades of colour and having a guaranteed stability against high temperatures. This problem is overcome by the present invention by a colorant having nanometric dimensions.

D1 is considered to represent the closest prior art.

The prior art does not give any indication to provide a ceramic colorant as defined in claim 1, in which the solvent of the suspension is a high-boiling alcohol. Therefore, an inventive step is acknowledged for the subject-matter of claim 1, of claims 2 to 4 which are dependent thereof and of use claims 9 to 11.

The combination of process features as defined in claims 6 and 7 is neither disclosed nor suggested by D1 to D4 of the prior art. Therefore, an inventive step is acknowledged for the subject-matter of claims 6 and 7.

The subject-matter of claims 5 and 8 is not novel, consequently also an inventive step has to be denied.

CLAIMS

1. Ceramic colorants in the form of suspensions of particles of colorant have nanometric dimensions in which the solvent of the suspension is a high-boiling alcohol.
- 5 2. The ceramic colorants according to Claim 1, in which the particles have dimensions of between 5 nm and 600 nm.
3. The colorants according to Claims 1 and 2, in which the high-boiling alcohol is chosen in the group consisting of diethylene glycol or ethylene glycol or polyethylene glycol.
- 10 4. The colorants according to Claims 1 to 3, in which the nanometric particles are chosen in the group consisting of:
 $M^{II}M^{III}_2O_4$, where M^{II} is chosen in the group consisting of Fe^{II} , Zn, Co, Ni, Mn, and M^{III} is chosen in the group consisting of Fe^{III} , Al, Cr, Mn,
 $CoAl_2O_4$, $Ti(Sb, Cr)O_2$, $(Zr, Pr)SiO_4$, $(Zr, V)SiO_4$, $(Al, Cr)_2O_3$, $(Al, Cr)MO_3$ (where $M = Y, Nd$,
15 $Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb$), $CaSn_{1-x}Cr_xSiO_5$, $Ti(Sb, Ni)O_2$, $(Zr, V)O_2$, $(Sn, V)O_2$,
 $Sn_{1-x}Cr_xO_{3-x/2}$ (where x is comprised between 0.01 and 0.1), Au^0 , Ag^0 , Cu^0 .
5. A process for the preparation of ceramic colorants according to Claims 1 to 4, in which:
 - to a known volume of alcohol there are added the salts of the desired metals, and the
 - 20 solution is then heated under stirring up to complete solubilization of the salts.
 - water is added in appropriate amounts for facilitating hydrolysis of the salts, and the solution is heated up to a temperature higher than 150°C.
 - once the reaction is completed, the suspension that has formed is left to cool to room temperature,
 - 25 - the suspension thus obtained is subjected to dialysis or ultrafiltration to eliminate the salts and/or to replace the solvent;
 - possibly the suspension is centrifuged, and the precipitate is collected and dried.
6. The process for the preparation of ceramic colorants according to Claims 1 to 4, in which:
30 there are rapidly added the reagents (solutions of salts of metals) to a polar solvent previously brought to the desired temperature of hydrolysis, and then the suspension is brought to room temperature, and the reaction environment is dehydrated with

dehydrating agents, then proceeding as specified in Claim 5.

7. The process for the preparation of ceramic colorants according to Claims 1 to 4, in which :

- the salts are dissolved in the high-boiling alcohol at an adequate temperature;
- 5 - an unmixable solvent is added to the high-boiling alcohol to form an emulsion of micelles of nanometric dimensions
- the necessary amount of water is added to the suspension under stirring, allowing it to react at a temperature higher than 120°C;
- it is then left to cool to room temperature, then proceeding as specified in Claim 5.

10 8. Colorants according to claims 1 and 2 in the form of powders, obtainable by the processes according to claims 5 – 7.

9. Use of the colorants according to Claims 1 to 4 for colouring ceramic materials, ceramic bodies, enamels.

15 10. Use of the colorants according to Claims 1 to 4 for colouring fabrics made of fibre or in a bolt.

11. Use of the colorants according to claims 1 – 4 in the catalyst and pharmaceutical field.